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THE EFFECTIVE NUCLEANT DURING THE GRAIN MODIFICATION OF TNT WIT--ETC(U)

MAY 79 M A PARRY , B W THORPE

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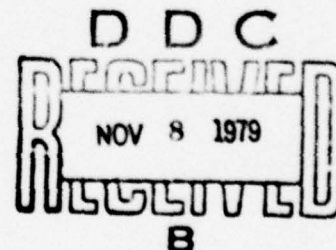
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THE EFFECTIVE NUCLEANT DURING THE GRAIN
MODIFICATION OF TNT WITH HNS

Murray A. Parry and Barry W. Thorpe

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10 Murray A. Parry and Barry W. Thorpe

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16. ABSTRACT (if this is security classified, the announcement of this report will be similarly classified):

Small concentrations of 2,2',4,4',6,6'-hexanitrostilbene (HNS) have been shown previously to modify the grain structure of 2,4,6-trinitrotoluene (TNT). At the very low concentrations used, the character and properties of the effective nucleant proved difficult to study and so an enrichment process has been developed. It is found that the nucleant is not the HNS which was added originally, but a complex of composition (TNT)₂ · HNS which is formed during thermal cycling of the individual components. The pre-production and simple addition of complex just prior to casting has been shown to be a feasible alternative to the cycle-cast technique currently being employed.

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THE EFFECTIVE NUCLEANT DURING THE GRAIN
MODIFICATION OF TNT WITH HNS

1. INTRODUCTION

2,4,6-trinitrotoluene (TNT) has physical and chemical properties which make it particularly suitable for the production of cast explosive formulations. Casts from TNT may, however, display undesirable characteristics of exudation, irreversible dimensional changes (1) and cracking in response to thermal stress. Cracks in the high explosive filling of a shell increase the likelihood of initiation and premature explosion under the extremely high forces encountered during gun firing.

2,2',4,4',6,6'-hexanitrostilbene (HNS) has been shown (2,3) to be an effective additive for the grain modification of TNT. Prevention of the growth of large, columnar grains of TNT with preferred orientation increases resistance to crack propagation and produces an isotropic TNT cast. In order to use HNS as an effective grain modifier for TNT, a cycle-cast method must be employed (3). A small concentration of HNS is heated in TNT to 100°C and the solution is stirred and then solidified. This mixture is then remelted with the constraint that the melt temperature should not exceed 85°C. Cooling this again to solidification produces a cast consisting of very fine randomly oriented grains.

We have previously described (4) the nucleation and solidification of TNT by the addition of HNS. There it was proposed that the effective nucleant was not the originally added HNS, but an associated complex of HNS and TNT which was deposited during the solidification of a supersaturated solution of HNS in TNT. From a 1% w/w solution of HNS in TNT and a two-stage thermal cycle, the nucleating material precipitates as a fine white solid which persists in TNT which is held liquid just above the melting point. At this low concentration the character and properties of the nucleant are difficult to study. This report describes methods by which it was attempted to isolate the nucleant in order that it could be characterized, and examines further this nucleation and growth phenomenon.

2. EXPERIMENTAL

Experimental work was undertaken to extract the nucleating material from the bulk TNT. Nucleant was prepared by a thermal cycle of 1% HNS in TNT and a number of enrichment techniques were then explored. The product was analysed by differential scanning calorimetry (DSC) and hot-stage microscopy. HNS and TNT of commercial purity and in a highly purified state were both used; none of the experimental results were affected by purity, except that the DSC peaks were sharper the higher the purity.

2.1 Materials

Commercial grade TNT was available locally with a purity of 99.7%. The commercial material was purified by the method of Gey, Dalbey and Van Dolah (5) to give a material with a melting point of 80.7°C. Gas chromatography showed that the purity of the material was greater than 99.95%.

Commercial grade HNS was prepared by Explosives Factory Maribyrnong according to the method of Shipp and Kaplan (6). Thin layer chromatography (TLC) showed that the material contained up to 5% of 2,2',4,4',6,6'-hexanitrobibenzyl (HNB), a by-product formed during the reaction. Commercial HNS was purified by the soxhlet extraction method of Syrop (7) and by recrystallisation from nitrobenzene. TLC showed that only trace quantities of HNB (<0.1%) remained. The purified HNS melted at 318°C.

Nucleant/TNT mixtures were prepared as follows. 500 g of 1% of HNS in TNT was heated in a stainless-steel kettle to 135°C, stirred for 1 hour (for complete HNS dissolution), filtered to remove extraneous matter and then cooled for solidification. To ensure that the efficient nucleant (4) was present prior to enrichment, small samples were taken from the bulk and examined by hot-stage microscopy. If the nucleation temperature was within 3°C of the melting point and the subsequent growth was fine-grained and had random orientation, the presence of the nucleant was confirmed.

2.2 Enrichment of Nucleant

Enrichment of the nucleant from the nucleant/TNT mixture was achieved by dissolution of TNT in suitable solvents and by molten TNT filtration. Acetone was chosen for initial enrichment studies because it readily dissolved TNT (109 g/100 g at 20°C and 600 g/100 g at 60°C) and therefore facilitated rapid enrichment. Chloroform was chosen as a milder enrichment medium. Molten TNT filtration was used to collect the nucleant in quantity for experimental casting.

2.2.1 Extraction with Acetone

50 g of a ground and sieved (212 μ m) mixture was soxhleted with acetone for 1 hour. The product in the thimble was dried and then analysed.

50 g of a ground and sieved mixture (212 μ m) was stirred rapidly in 100 ml acetone for 2 minutes at 20°C. The undissolved product was filtered, dried and then analysed.

2.2.2 Molten TNT Filtration

The nucleant/TNT mixture was reheated in the stainless-steel kettle and the melt temperature recorded and controlled so that at no time during the remelt period did the temperature exceed 85°C, following the example of reference (3). When all the TNT was molten the mixture was poured through a heated, powder-funnel delivery-tube system in the hot-box apparatus illustrated in Figure 1, and filtered. The main components of the modified laboratory-filtration apparatus were as follows. The heat source was an IR lamp controlled by a proportional temperature-controller. Temperature was measured by a digital thermometer and uniformity was assisted by an air-driven paddle stirrer. The filter funnel was of the Hirsch type because of the relatively small quantity of solid in comparison to the volume of molten TNT to be filtered. The filter paper was synthetic cellulose which had good thermal resistance and was compatible with molten TNT. A silastic cover for the funnel increased the filtration rate and stopped splashing. The solid product collected from each successive filtration weighed between 8-11 g. The molten TNT filtrate was then poured from the filtration flask into the stainless-steel kettle. Assuming that the original 5 g of HNS had all been converted to nucleant and filtered off, a further 5 g of HNS would need to be added to repeat the cycle. However, it was found that this would not dissolve completely in the filtrate after stirring for one hour at 135°C. Clearly, some HNS had remained in solution during the filtration; it was found that about 1 g of HNS had passed through in this way, so only 4 g of HNS was added for successive cycles. For ten cycles of the 500 g batch of TNT, 41 g of HNS was added and approximately 100 g of the nucleant/TNT product was obtained. For each filtration the hot-box was allowed to stabilise at 85°C for 2 hours.

2.2.3 Cold Chloroform Washing

30 g of a ground and sieved mixture (212 μ m) was stirred rapidly in 200 ml of chloroform at 20°C for either 1, 2, 5, 30 or 60 minutes. For each wash the undissolved product was filtered, dried, and then analysed.

2.3 Analysis of Enriched Nucleant by DSC and Hot-stage Microscopy

Thermal measurements were made using a Perkin Elmer DSC-1B differential scanning calorimeter (DSC). The DSC provides a sensitive measure of the temperature and enthalpy of a transition or reaction. Heating and cooling rates were varied from 8°C/min to 64°C/min. Ordinate sensitivity was varied depending on experimental conditions such as sample size and heating rate.

Samples were heated from 20°C through the melting point of pure HNS (318°C). The success of each enrichment technique could be rapidly assessed by monitoring the amount of TNT which was left in the enriched sample.

Microscope observations were made using a standard Leitz 'Ortholux' microscope with an attached Mettler FP2 hot-stage. Samples were heated and cooled at 2°C/min.

2.4 Casting and Mechanical Testing

1% of the enriched nucleant was added to molten TNT at 85°C, stirred for 5 minutes and cast into a 63 mm diameter mould. For comparison, a cast of TNT was prepared. Both casts were sectioned longitudinally. One half of each was polished (8) for visual examination. The other half was machined into cylinders for mechanical testing. An Instron Universal Testing machine was used to measure the compressive and tensile strength of both casts at 20°C.

3. RESULTS AND DISCUSSION

3.1 Extraction of Nucleant

The acetone soxhlet extraction method failed to extract the nucleant from the nucleant/TNT mixture. When the solid residue from this extraction was examined by DSC, the DSC curve of HNS was obtained. Figure 2(a) shows the thermal behaviour of HNS; an endothermic fusion peak beginning at 318°C which is overtaken by the exothermic thermal decomposition. Figure 2(b) shows the thermal behaviour of TNT with a fusion peak occurring at 80.7°C and decomposition at 290°C. The residue from soxhlet extraction also failed the test for the presence of the highly active nucleant; molten TNT on a microscope slide undercooled by about 6°C before nucleation occurred at only a few sites (4).

Cold acetone washing succeeded as an extraction method. Heating the extraction residue gave a DSC curve with an additional, broad, endothermic peak at 107-123°C (Figure 2(c)). This residue acted as a highly active nucleant for TNT. Molten TNT filtration also preserved and enriched the nucleant.

3.2 Characterisation of Nucleant

An endothermic process occurring at a temperature between the melting points of a binary system may be interpreted in a number of ways; the fusion or dissociation of a molecular complex, the fusion or transformation of a polymorph, or the fusion of a solid-solution could all account for the observed endothermic peak. The following DSC and microscope studies provide a strong indication that the nucleant is a TNT/HNS complex.

Hot stage microscopy was used to examine the nucleant enriched by acetone washing. When a sample of the nucleant is heated at 2°C/min to 82°C (Figure 3), molten droplets are observed; clearly, this is TNT in the sample melting, the first endotherm in the DSC curve of Figure 2(c). Further molten material appears at about 110°C; this corresponds closely with the beginning of the second endotherm of Figure 2(c). The production of molten material continues with further heating until at about 125°C (Figure 4) a large part of the sample is molten. This stage corresponds to the broad endotherm and demonstrates the release of a liquid product - considered to be TNT. Observation through crossed-polars (Figure 5) makes it clear that a dispersed solid remains in the molten medium. Further heating causes no noticeable change in the solid until vaporisation and decomposition cause obscuration of the microscope field. This dispersed solid is HNS.

DSC experiments were carried out to examine the reversibility of the endothermic process and to confirm that the liquid product released during the process was TNT. Figure 6(a) shows the DSC curve of the enriched nucleant where the heating scan was interrupted at a temperature above the broad endotherm. Peak A represents the fusion of TNT and peak B the endothermic process. On cooling to solidification and reheating the same sample (Figure 6(b)), peak B does not reappear and the TNT fusion peak C is much larger in area than peak A.

These results indicate that the nucleant is a TNT/HNS complex. It is clearly not a HNS polymorph, since the reheat DSC curve 6(b) and microscope observations show that, during the endothermic process, TNT is produced. Since the nucleant was produced as a solid as the TNT solidified (2,4), it is extremely unlikely that it is a polymorph of TNT formed at the same time and in contact with the known (9,10) stable form. The fact that the nucleant is not a conventional solid solution is shown by its absence on reheat in Figure 6(b). The complex has dissociated on heating into liquid TNT and solid HNS.

3.3 Molecular Complexes

The formation of molecular complexes resulting from the interactions of molecules is a widespread chemical phenomenon (11-14). The association of two components occurs in a definite stoichiometric ratio and the interaction is somewhat stronger than ordinary Van der Waals associations. No such interaction between TNT and HNS has been reported previously although each component individually has been shown to form molecular complexes. For example, TNT complexes with benzene (15), alkali-metal alkoxides (16,17) and amines (18). The preparation and properties of a series of complexes of HNS with some 47 compounds (mainly aromatic amines and phenols) has also been reported (19). The existence of a TNT/HNS complex is somewhat unexpected since the components are both classed as strong electron acceptors in these interactions. Together they would appear to offer little possibility for a strong donor-acceptor interaction. Interactions have been reported, however, between pairs of nitro-containing compounds which are very strong acceptors (for example, picric acid interacts with dinitrotoluene, dinitrobenzene and 2,4,6-TNT) (20). Therefore nitro compounds may form loose molecular complexes, not only with electron donors, but also with other nitro compounds. The stability of complexes between two nitro compounds (without other predominating donor-acceptor forces) has been attributed to electrostatic forces resulting from the strong local dipole moment of each nitro group plus dispersion forces (21). So, although HNS and TNT are both classed as electron acceptors, we cannot preclude the formation of a loose molecular complex by electrostatic attraction of the two molecules.

3.4 Composition of the Complex

The enrichment of the TNT/HNS complex by washing with cold acetone is only suitable for the preparation of small quantities in the laboratory. In order to produce the quantities needed for use in experimental castings, the technique of molten TNT filtration was used. This enabled enrichment from the 1% of HNS added originally to a mixture containing 70% complex : 30% TNT, shown by measurement of the areas under DSC peaks such as those in Figure 6. Heating the complex causes it to dissociate to molten TNT and solid HNS, though more work is needed to describe precisely the conditions under which

breakdown of the complex occurs. It appears that the dissociation is direct, as only a single peak is obtained from DSC. Nor does significant recombination occur after the enriched nucleant is broken down, since peak B does not reappear in Figure 6(b).

Interpretation of the data from the DSC curves shown in Figure 6 (see Appendix 1) produced an estimate of the complex composition of 1.6 TNT : HNS (molar ratio), suggesting a complex 3:2 or 2:1 or perhaps a range of different compositions. However, it was recognised that partial dissociation of the complex might have occurred prior to DSC analysis, during the filtration at 85°C, or by the use of a polar solvent such as acetone.

In order to test for this possible dissociation, chloroform was used as a milder enriching solvent. The solubility of TNT in chloroform at 20°C is lower than in acetone. Chloroform also has a much lower dielectric constant than acetone. DSC results showed that the amount of TNT left in the enriched sample varied, and the calculated complex composition decreased, as the washing time in chloroform increased (Table 1).

TABLE 1

EFFECT OF CHLOROFORM WASHING ON 212 μ m COMPLEX/TNT

Wash Time (min)	Molar Ratio $\frac{\text{TNT}}{\text{HNS}}$: 1	% TNT
1	2.00 ± 0.06	33 ± 14
2	1.92 ± 0.11	11 ± 3
5	1.94 ± 0.05	6 ± 2
30	1.77 ± 0.06	11 ± 1
60	1.66 ± 0.03	9 ± 1

In the light of these results, we assign the value of 2 to this molar ratio, making the complex $(\text{TNT})_2 \cdot \text{HNS}$. Washing for extended periods with chloroform, using a harsher solvent such as acetone or removing the bulk of the TNT from the complex/TNT mixture by filtration at 85°C, all cause partial dissociation of the complex. The enthalpy of dissociation of the complex was calculated at 28 kJ/mol (using DSC results of residue from 1 minute chloroform washing). This value is much lower than the transformation enthalpies reported for the dissociation of a range of other solid HNS complexes (19). In addition, the complex required only one DSC heating scan through the endothermic peak to cause full dissociation. Other complexes may undergo repeated heating-cooling cycles on the DSC with little or no dissociation (22,23). From these two observations we predict a relatively low thermal stability for $(\text{TNT})_2 \cdot \text{HNS}$.

3.5 Mechanical Testing

Use of the additive HNS in TNT-based castings is known to produce an increase in mechanical strength. In order to confirm that the complex extracted from HNS/TNT produces the same grain refinement in TNT as the cycle-cast method, pre-produced complex was added to molten TNT during casting. Molten TNT filtration was used to produce the enriched complex in quantity for this experimental casting.

Table 2 shows the results of cast TNT with pre-produced complex compared with normal cast TNT. The mechanical strength is increased to the same degree as casts produced by the cycle-cast method (24). The modified grain structure seen in Figure 7(b) and the strength of the modified TNT cast confirm that the enriched material is the effective grain modifier produced during the cycle-cast method. The modified cast consists of very fine, randomly oriented TNT grains, both in the chilled layer region and throughout the bulk of the TNT matrix. This is in complete contrast to the normal TNT cast with its characteristic spherulite structure in the chilled layer (25) and its large, aligned TNT grains in the bulk of the material (Figure 7(a)).

T A B L E 2

MECHANICAL TESTING OF TNT AND MODIFIED TNT CASTS

Cast *	Mode of Test ⁺	
	Tension	Compression
(A) TNT	0.3 MPa	2.9 MPa
(B) Modified TNT	1.5 MPa	10.5 MPa

* axes of cylinders machined parallel to axis of cast.

+ tested at 20°C, with strain rate of 0.01 min⁻¹ for tension and 0.04 min⁻¹ for compression.

4. CONCLUSIONS

It can now be more clearly understood why a temperature cycle is required to provide HNS with its exceptional ability to nucleate TNT. The nucleant, a complex of composition $(\text{TNT})_2 \cdot \text{HNS}$, forms in solution above the melting point of TNT. The first heating cycle of the cycle-cast method is required to dissolve the HNS. It has been reported previously (2,4) that the complex precipitates during the solidification of TNT, as shown by the striated appearance of the deposit. This precipitation during the first cooling cycle allows a wide dispersal of solid complex which, on further cycling, enables nucleation to occur at a large number of sites.

The complex has, apparently, a low thermal stability. As an enriched mixture with TNT, it dissociates above 107°C . As an additive to a large quantity of molten TNT it appears even less stable, as indicated by the constraint of 85°C on the re-melt temperature of the cycle-cast method. Isothermal experiments to monitor the dissociation rate are required to ascertain the thermal stability of the complex. Pre-production of the $(\text{TNT})_2 \cdot \text{HNS}$ complex offers a single stage casting process and may enable a relaxation of the maximum melt temperature.

This report has illustrated a series of enrichment techniques which have been used to prove the existence of a TNT/HNS complex. The molar composition has been estimated as $(\text{TNT})_2 \cdot \text{HNS}$ and the transformation enthalpy on dissociation has been calculated at 28 kJ/mol . HNS is added at a concentration of 1% and complex has been produced at a purity of greater than 90%. The cycle-cast technique can now be explained in terms of complex formation, complex stability and grain modification of TNT by a $(\text{TNT})_2 \cdot \text{HNS}$ nucleating species, and not the HNS which was originally added. An alternative technique for the grain modification of TNT, the pre-production and addition of complex just prior to casting, has been shown to be feasible.

5. ACKNOWLEDGEMENTS

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APPENDIX 1

After interpretation of the data from the DSC peaks of Figure 6(a) and 6(b) the complex composition can be estimated.

- mS = mass of DSC sample
- mT_i = mass of TNT in the sample before heating, Figure 6(a)
- $m(T^*H^*)$ = mass of TNT/HNS complex
- mH^* = mass of HNS released on complex dissociation
- mT^* = mass of TNT released on complex dissociation
- mT_f = mass of TNT melting Figure 6(b)

If we assume that all HNS originally added was converted to nucleant and that the enrichment technique did not cause any partial dissociation prior to DSC analysis then,

$$mS = mT_i + m(T^*H^*)$$

After complete dissociation of the complex the reheat in Figure 6(b) has only TNT and HNS present.

$$mS = mH^* + mT_f \text{ where } mT_f = mT_i + mT^*$$

The complex composition is given by,

$$\frac{mT^*}{227} \text{ TNT} : \frac{mH^*}{450} \text{ HNS}$$

$$\frac{mT_f - mT_i}{227} \cdot \frac{450}{mS - mT_f} \text{ TNT} : \text{HNS}$$

Since we accurately know the sample mass and the represented mass of TNT melting under the peaks A and C of Figures 6(a) and (b), we can easily obtain a value for the complex composition.

However if the DSC samples are in any way contaminated the value is no longer accurate. The presence of free HNS (which may have formed during enrichment of the nucleant as a result of partial dissociation) will lower the calculated composition.

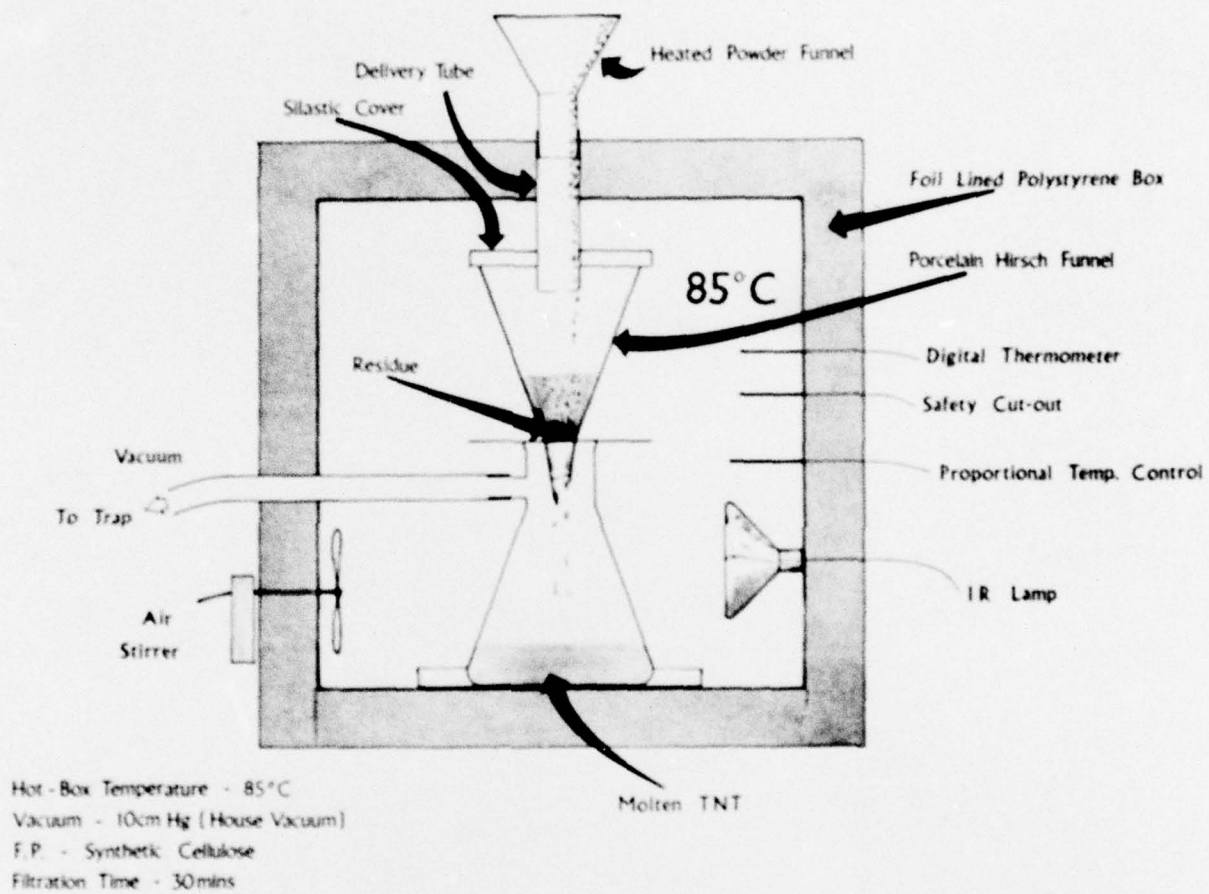


FIG. 1 - Hot-box for Filtration of Molten TNT.

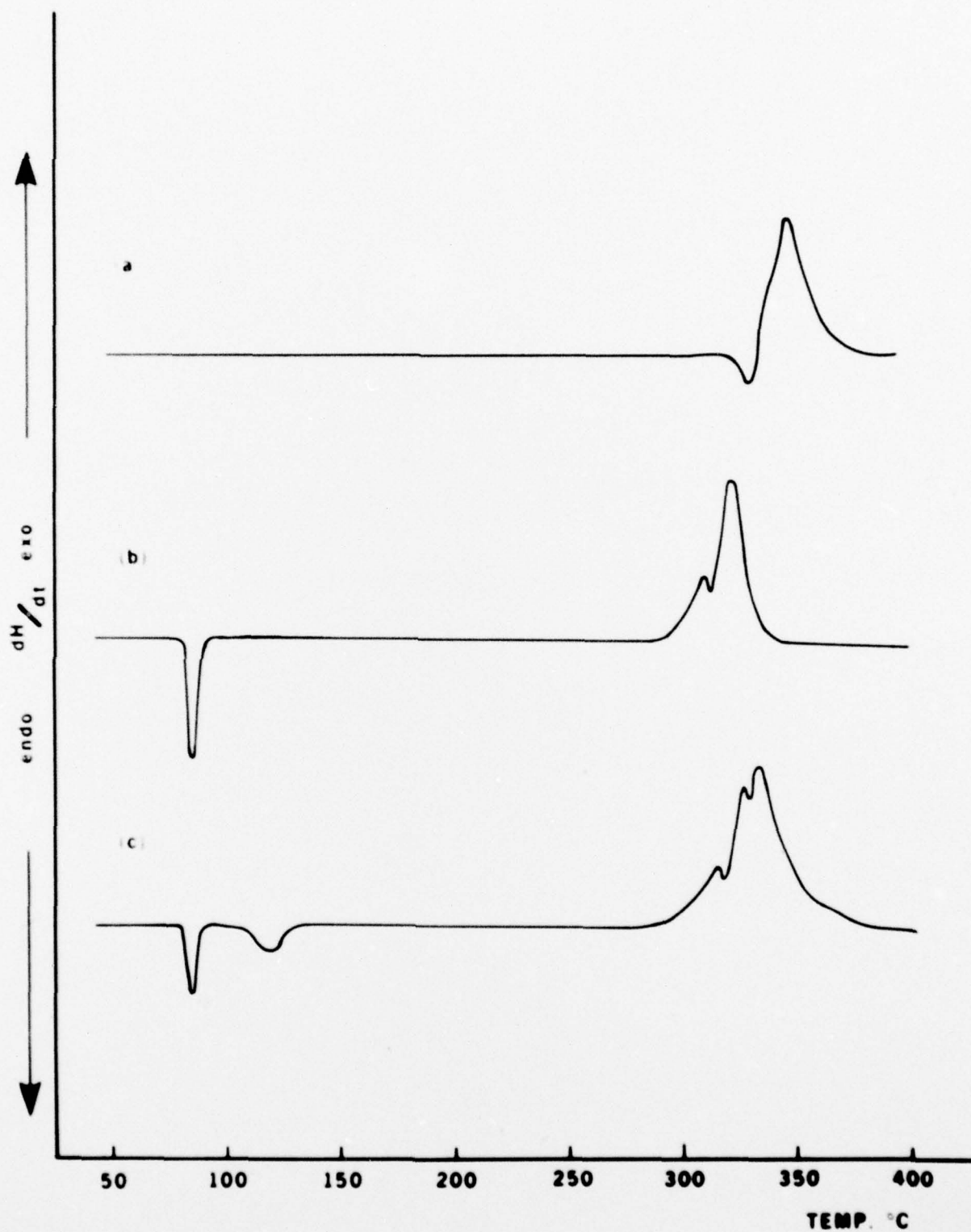


FIG. 2 - DSC curves of (a) HNS, (b) TNT, (c) Enriched Nucleant.

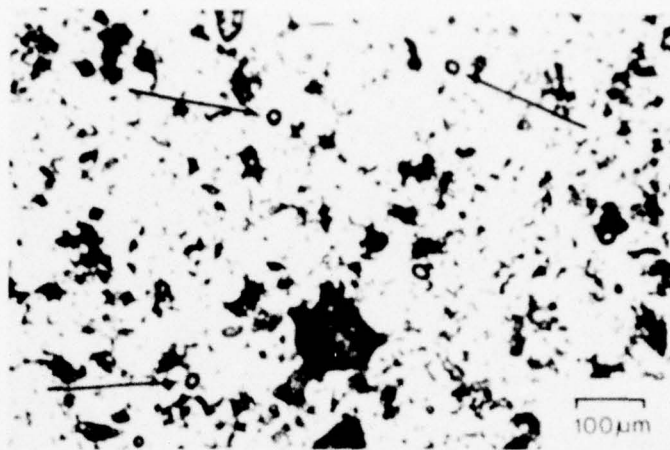


FIG. 3 - Enriched Nucleant in Powder Form (Dark Areas) with Droplets of TNT at 82°C (Some Arrowed). White Area is Transmitted Light.

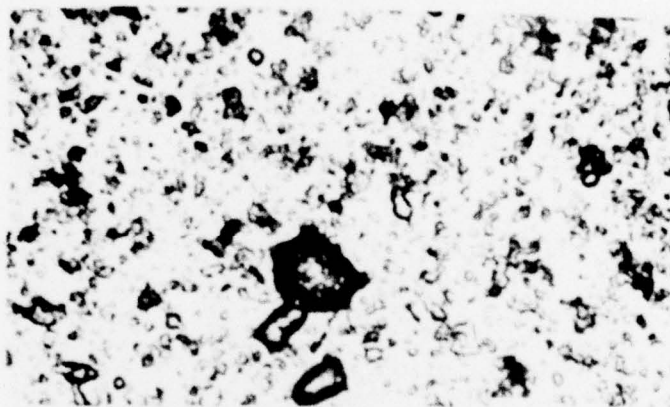


FIG. 4 - Material of Figure 3 after Heating to 125°C. Nucleant has dissociated to Liquid TNT and Solid HNS.



FIG. 5 - Same Area as Figure 4 through Crossed Polaroids. Solid HNS is visible.

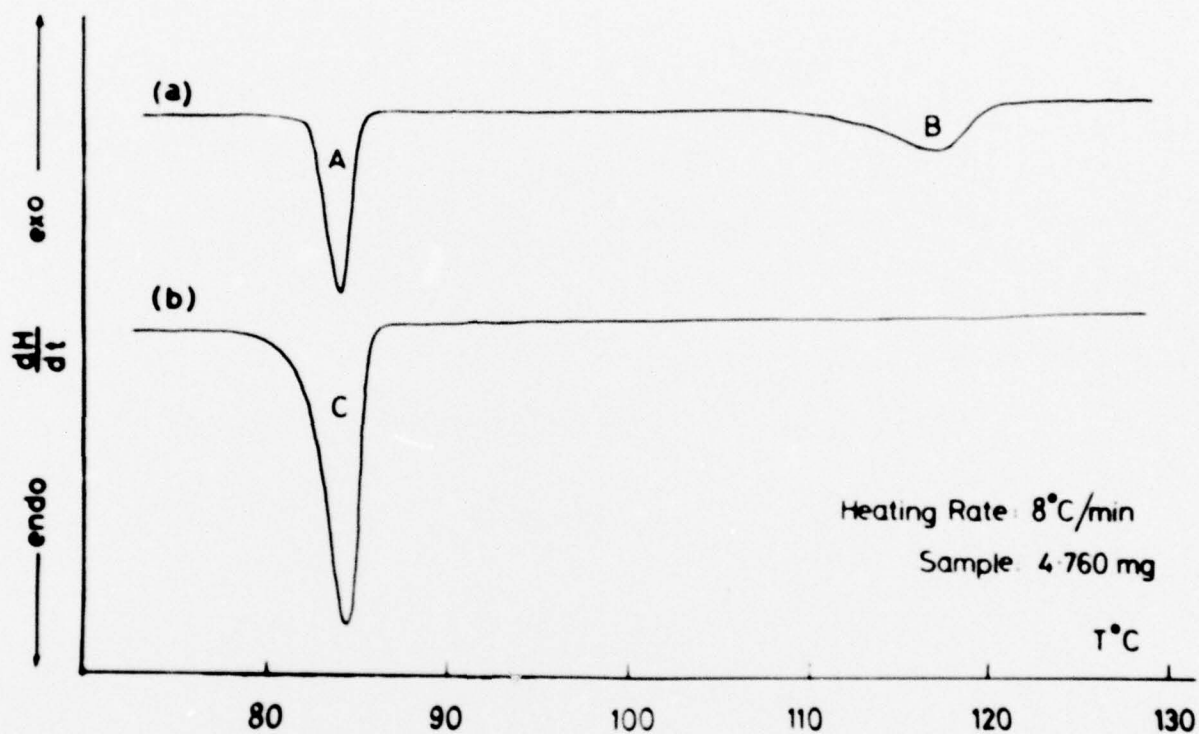


FIG. 6 - DSC Curves of (a) Enriched Nucleant, (b) Same Sample after Solidification and Reheat.

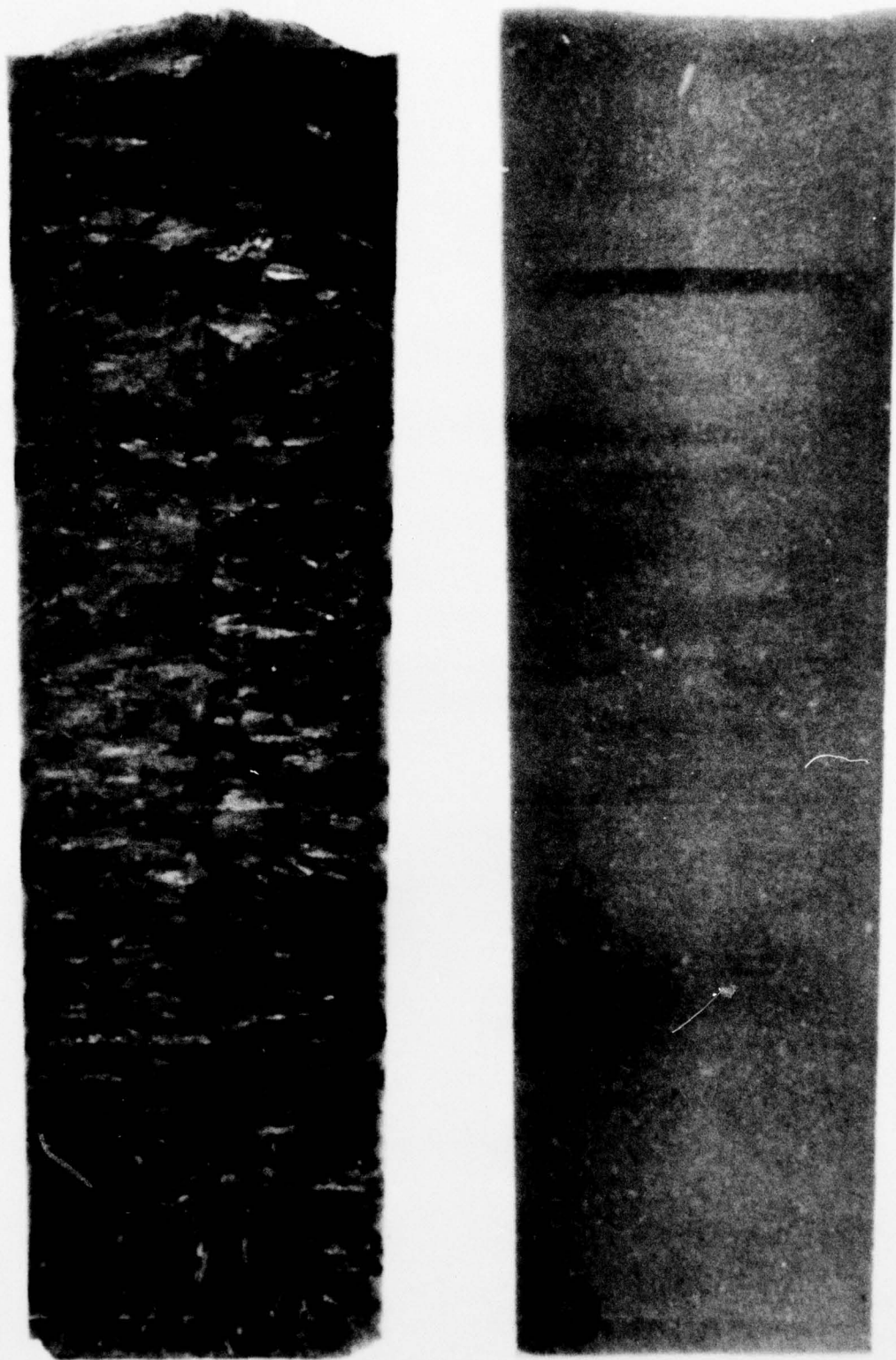


FIG. 7 - Casts of (a) TNT, (b) Modified TNT.

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